# Magnetic properties of $TlCu_{2-x}Fe_xSe_2$ crystals

S. Felton[a] and P. Nordblad
*Department of Engineering Sciences, Uppsala University, P.O. Box 534, SE-751 21 Uppsala, Sweden*

S. Ronneteg and R. Berger
*Department of Materials Chemistry, Uppsala University, P.O. Box 538, SE-751 21 Uppsala, Sweden*

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The magnetic properties of two compositions of random solutions in the $TlCu_{2-x}Fe_xSe_2$ system with $x=0.2$ and 0.45 have been investigated by superconducting quantum interference device magnetometry. The crystal structure is of a layer type and ordering due to the iron atoms occurs at low temperatures, with $T_c=85$ K for $x=0.2$ and $T_c=130$ K for $x=0.45$. The samples were highly textured crystals and the magnetic moments of both compositions were found to align along the $c$ axis of the structure. The saturation moments were found to be $1.5\mu_B$/Fe for $x=0.2$ and $0.66\mu_B$/Fe for $x=0.45$. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1854434]

## I. INTRODUCTION

Layered magnetic structures are of great technological and scientific interest. They can be artificially manufactured, such as multilayers, or be thermodynamically stable crystal structures, as in the case of $TlCu_{2-x}Fe_xSe_2$. An advantage of studying crystal structures is that they contain less stress and defects than artificial systems. This means a better control over the factors that determine the magnetic properties of the systems. Crystals with layered magnetic structure are therefore important model systems.

The magnetic properties of two compositions of the layered $TlCu_{2-x}Fe_xSe_2$ structure, with $x=0.2$ and $x=0.45$, have been investigated for this paper. The parent compound $TlCu_2Se_2$ is a nonmagnetic metal with tetragonal symmetry where the Cu atoms form layers, described by a square sublattice. Substituting Fe for Cu in this range does not change the symmetry of the system, so that the Fe atoms are situated in well defined layers separated by nonmagnetic material. For these concentrations of Fe the samples are fairly dilute magnetic alloys, showing cooperative phenomena of either ferromagnetic or ferrimagnetic character. A previous study on $TlCu_{2-x}Fe_xSe_2$ (Ref. 1) was made using powder samples. The presence of very small amounts of $Fe_3O_4$ meant that ferrimagnetic contributions had to be subtracted from the results through a series of field-dependent measurements. This created uncertainties in values of moments and transition temperatures as discussed in Ref. 1.

The samples studied in this paper were highly textured crystals, since one of the interesting questions was whether the magnetic moments lie in the plane of the layers or out of it. According to previous reports on this type of structure the magnetic moments can be either perpendicular to the $c$ axis, as for $TlCo_2Se_2$ (Refs. 2 and 3) and $TlCo_2S_2$,[4] or parallel to it, as for $TlFe_{2-x}Se_2$ $x=0.3-0.4$, with and without vacancy ordering.[5,6] Studying crystals instead of powder samples also decreases the amount of oxide impurities, and hence increases the accuracy of the measurements.

[a]Author to whom correspondence should be addressed; electronic mail: solveig.felton@angstrom.uu.se

## II. EXPERIMENT

The crystals of nominal composition $x=0.2$ and $x=0.45$ were synthesized by mixing stoichiometric amounts of TlSe, Se, Fe, and Cu in evacuated silica tubes and the cell parameters of the final products were checked by x-ray powder diffraction. The highly textured crystals were flat with faces of the (001) orientation. The $x=0.2$ sample used for the magnetic measurements had a mass of 8.0 mg and the $x=0.45$ sample had a mass of 10.4 mg.

The magnetization of the samples was measured on changing the temperature for a fixed applied field, or on changing the applied field for a fixed temperature. These measurements were made with the applied field either parallel or perpendicular to the $c$ axis of the tetragonal cell. For the magnetization versus temperature measurements two different protocols were used for all samples: zero field cooled (zfc) and field cooled (fc). In the zfc protocol the sample is cooled to the starting temperature with no applied field. Then the field, in all cases 100 G, is applied and the data are collected on heating the sample. In the fc protocol the desired measurement field is applied at a temperature above the transition temperature of the sample and the sample is cooled to the starting temperature in this field. The data are then collected on heating the sample, as for the zfc protocol.

The maximum applied field of the equipment was 50 kG. All magnetic measurements were made using a superconducting quantum interference device magnetometer of the type quantum design, MPMS XL. The magnetization versus applied field measurements were made at 10 K for both directions of both compositions.

## III. RESULTS

The cell parameters show a linear trend versus the amount of substituted Fe up to $x=0.5$.[1] For the two compositions studied in this paper the cell parameters were determined from x-ray powder diffraction measurements. This yielded $a=3.892$ Å and $c=13.938$ Å for the $x=0.20$, and $a=3.957$ Å and $c=13.754$ Å for the $x=0.45$ sample. The cell parameters for the $x=0.45$ sample agree well with those re-

 

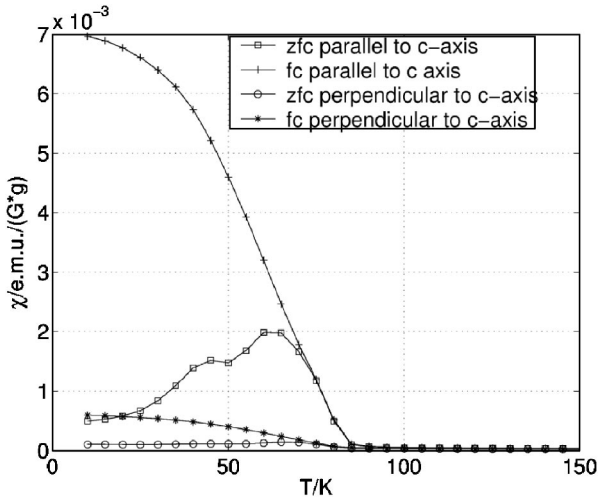


FIG. 1. The susceptibility of the $x=0.2$ sample as a function of temperature. Note that the zfc and the fc curves for the two measured directions coincide for $T \geqslant 85$ K.

ported in Ref. 1, while there is a significant deviation for the $x=0.20$ sample. The true composition is more likely $x=0.16$ if Vegard's law is followed.

The susceptibility as a function of temperature measured parallel and perpendicular to the *c* axis of the structure is shown in Fig. 1 for $x=0.2$ and in Fig. 2 for $x=0.45$. As can be seen from these figures both compositions form magnetically ordered structures at low temperatures, with $T_c=85$ K for $x=0.2$. The $x=0.45$ sample shows a more complex temperature dependent magnetization behavior with two transition temperatures, at 80 K and 130 K. This can be seen in the inset of Fig. 2 which shows an enlargement of the susceptibility versus temperature curve for $x=0.45$ measured parallel to the *c* axis. Both transitions are present for both measurement directions. The transition at 130 K is weak compared to the one at 80 K. No such extra transition is found in the corresponding curves for the $x=0.2$ sample.

From the paramagnetic susceptibility it is possible to determine the effective moment of the magnetic atoms of a structure assuming a Curie–Weiss law behavior. This analysis yielded a $p_{\text{eff}}$ of approximately $1\mu_B$/Fe for $x=0.2$ and $0.5\mu_B$/Fe for $x=0.45$.

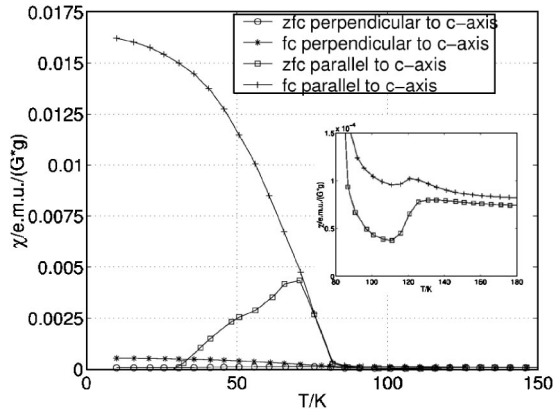


FIG. 2. The susceptibility of the $x=0.45$ sample as a function of temperature. The inset shows an enlargement of the curves measured parallel to the *c* axis for 80 K$\leqslant T \leqslant$180 K where the transition at $T=130$ K can be seen.

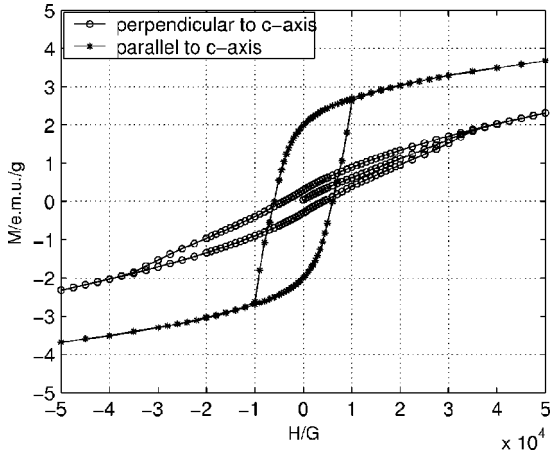


FIG. 3. The magnetization of the $x=0.2$ sample as a function of applied field at $T=10$ K.

For both compositions the magnetic moments were interpreted to align along the *c* axis of the structure giving an out-of-plane magnetization of the layers. The net moment per Fe atom in the ordered phase was determined from magnetization versus field measurements at 10 K, see Figs. 3 and 4 for the $x=0.2$ and the $x=0.45$ sample, respectively. Neither of the compositions reached full saturation at the maximum field of the equipment, 50 kG, but the slope of the curves levels off for the out-of-plane directions, allowing us to make an estimate of the saturation moment. This yields $1.5\mu_B$/Fe for $x=0.16$ and $0.66\mu_B$/Fe for $x=0.45$.

## IV. DISCUSSION

The investigated material consists of single-crystal aggregates of a strong sheet habit, where the *c* axis forms the normal to the prominent crystal faces. This means that the *c*-axis orientation is common for the measured material, even if the *a* and *b* axes are not. The magnetic moments of both compositions seem to align parallel with the *c* axis in the ordered phase. This was not unexpected, since it has previously been found that the magnetic moments of $TlFe_{2-x}Se_2$ ($x=0.3$–$0.4$) lie along the *c* axis.[5,6] Figures 1 and 2, as well

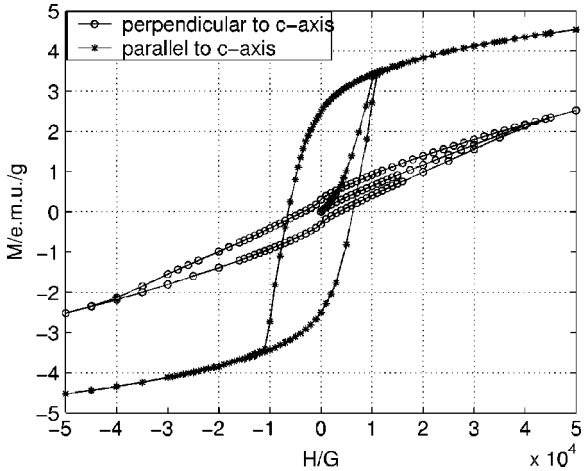


FIG. 4. The magnetization of the $x=0.45$ sample as a function of applied field at $T=10$ K.

as 3 and 4, all show that the susceptibility is markedly higher for the orientation of the field parallel to the *c* axis. Thus, there is a strong indication that there is a net moment along the *c* axis. However, the data do not allow us to say that the moments lie completely parallel with this axis; we cannot completely rule out the presence of a fan structure without neutron data for support.

At present we have no explanation for the appearance of an extra transition in the susceptibility versus temperature curve for $x=0.45$. Further measurements of the field dependence of the magnetization should be carried out around 70–130 K.

The paramagnetic effective moments of both compositions appear to approximately follow a Curie–Weiss law behavior. The values of the moments are however much smaller than those expected from free spins corresponding to Fe $d^5$. This is in agreement with what was reported in Ref. 1.

The saturation moments reported here are in reasonable agreement with previous findings on powders in Ref. 1. The data from the powder measurements are by necessity connected with large uncertainties, due to the corrections made because of the presence of $Fe_3O_4$ in those samples, so that perfect agreement with these data is not expected.

The magnetization versus temperature curves for the highly textured crystals differ significantly from those for powders presented in Ref. 1. We find a rather large hysteresis in our samples, while the powder samples showed none. This may be due to the fact that large crystals always contain domain walls, whereas the powder samples of Ref. 1 probably did not. The hysteresis curves show a clear twofold symmetry centered on the origin. The high field branch of the hysteresis curves for both compositions has a slope that is practically independent of the measurement direction. This indicates that there is a paramagnetic component to the susceptibility even at low temperatures.

The samples studied are fairly diluted solid solutions of a spin-carrying species within a Pauli paramagnetic matrix, $TlCu_{2-x}Fe_xSe_2$. The *x* values studied here, 0.2 and 0.45, thus represent a situation where, respectively, 10% and 22.5% of the copper sites of the host structure contain $Fe^{3+}$ in a random way. These concentrations lie below the percolation limit of 29% for next-next nearest neighbor exchange interactions in a square lattice.[7] As an effect of this, each transition metal layer (containing iron and copper mixed) may contain iron clusters of various sizes that lie isolated from one another in each layer, and without proper matching towards clusters in adjacent ones. This may very well be an explanation why there is still a paramagnetic component. As for any paramagnetic system, only extremely high fields (and low temperatures) may bring about a saturation of this component. This investigation cannot give any clue to the cluster size distribution which, moreover, might be sensitive to the thermal history of the samples.

## ACKNOWLEDGMENTS

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